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SUBJECT: Summary of Dioxin Data Evaluation for the Santa Susana Field Laboratory, 5800 Woolsey Canyon Road, Canoga Park, California

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At the request of the Department of Energy (DOE), the California Department of Toxic Substances Control (DTSC) evaluated the quality of dioxin data collected from selected DOE RCRA Facility Investigation (RFI) site locations at the Santa Susana Field Laboratory (SSFL) to determine how these data should enter into calculation of sample-specific dioxin-toxicity equivalents (dioxin-TEQs). A dioxin-TEQ expresses the concentration of dioxin-related compounds in a soil sample as the sum of the product of their individual concentrations multiplied by their relative toxicities. These toxicities are expressed relative to that of 2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD), the most toxic and best characterized of the dioxins. Dioxin-related cleanup decisions can thus be made based on the total TCDD-toxicity equivalents present in a sample. Specific questions about the data and recommendations as to how they should be used are addressed below. DTSC also reviewed the existing Lookup Table (LUT) dioxin-TEQ value in light of these recommendations (DTSC, 2013).

Background

The original goal of this memorandum was to respond to CDM Smith's (CDM) request for guidance on how to represent Estimated Maximum Possible Concentration (EMPC)-qualified dioxin/furan soil analytical data for the purpose of calculating Site sample dioxin-TEQs. USEPA Method 1613B is commonly used to quantitate soil concentrations of tetra- through octa-chlorinated dibenzo-p-dioxins (CDDs) and dibenzofurans (CDFs), especially seventeen CDDs and CDFs that are chlorinated on the 2,3,7 and 8 positions. These compounds, often referred to as dioxin and furan "congeners," differ from one another in the number and location of bonded chlorine

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atoms. Although 75 CDDs and 135 CDFs exist, it is those congeners that contain a common structure of chlorine atoms at the 2,3,7 and 8 positions of the dibenzo-p-dioxin ring and the dibenzofuran ring that have the highest affinity for the aryl hydrocarbon receptor (Ah-R). The Ah-R is a cytosolic receptor found in most vertebrate tissues that is thought to mediate most, if not all, toxic effects of dioxin/furan congeners, including carcinogenicity (Beischlag et al, 2008). Data from experimental mixtures of dioxin congeners are consistent with additivity of their toxic effects. Of these congeners, TCDD is the most potent carcinogen. As a result of their additive toxicities, dioxin congener levels in a media sample are normally expressed relative to that of TCDD, where the total dioxin-TEQ is calculated by summing the products of each congener concentration multiplied by its Toxic Equivalency Factor (TEF). The TEF represents the toxicological potency of a congener relative to the potency of TCDD. Mammalian TEF values were most recently updated by the World Health Organization in 2006 (WHO; Van den Berg et al, 2006).

Specific Questions and Recommendations Concerning Use of Dioxin Data:

(1) **How are qualified dioxin data that are EMPC-flagged to be evaluated in calculation of soil sample dioxin-TEQs?** The DTSC-SSFL technical team conferred with our dioxin chemist at the DTSC Environmental Chemistry Laboratory (ECL) and learned that gas chromatograph/mass spectrograph dioxin data that do not coincide with an acceptable range of ion abundance ratios (ie, mass:charge ratios for a set of primary and secondary congener ions) are often qualified as EMPC data. EMPC data are often shown in laboratory reports with an associated "J" designation (referred to as a "J-flag"), meaning that this is an estimated value. Interferences within a sample often cause the ion mass ratio to be offset. According to USEPA's National Functional Guidelines (NFGs), an ion abundance (ratio) outside the criteria does not unequivocally prove that dioxins/furans are or are not present (Section IX in USEPA, 2011). It only indicates that either "an interference is present for one of the ions, or that another compound may be present." In addition, there is uncertainty as to the true identity of an EMPC-qualified congener. This uncertainty could potentially lead to an increase in false positives, in that additional dioxin-TEQ samples could be determined to exceed the LUT dioxin-TEQ value when they actually are not the dioxin congeners being compared to. As discussed below, one way to constrain this uncertainty is to use zero for the EMPC value when calculating the sample dioxin-TEQ. The NFG guidelines state that standard qualifiers such as "U" or "J" may not be appropriate for these data, and that the reviewer should rely on professional judgment and organization policy to decide how to qualify EMPCs. Based on this information, the DTSC-SSFL technical team concluded that we could not rely on EMPC-qualified data to truly indicate the presence of a dioxin/furan congener, let alone its actual concentration.

According to the NFGs, there are two common approaches for calculating the dioxin-TEQ for a sample (p 40 of NFG, 2011). In the first approach, only those 2,3,7,8-substituted CDD and CDF congeners that were detected and that meet all of the qualitative identification criteria are used. A zero is used for any EMPC or EDL

values in the dioxin-TEQ calculations. In the second approach, the reported EMPC and EDL values are included as surrogates for the non-detect results, along with positively identified 2,3,7,8-substituted CDD and CDF congeners for calculation of the dioxin-TEQ. Whichever approach is used, it is recommended that one consider the impact of using estimated quantities (including J-flagged results, EMPCs, etc) in the TEQ calculation.

To determine whether using zero for EMPC values during calculation of Site sample TEQs influenced the amount of sample TEQs that exceeded the LUT dioxin-TEQ, the Human and Ecological Risk Office (HERO) at DTSC evaluated 100 Site soil samples from DOE Subarea-5D (SA-5D) using two different methods. One set of SA-5D dioxin-TEQs were calculated by setting all "undetected" values (ie, U-, QU-, UJ- and QUJ-qualified results where "Q" was used to denote an EMPC) equal to the Estimated Detection Limit (EDL), and setting EMPC results (ie, QJ-qualified data) equal to the reported EMPC value. The second set of Site sample dioxin-TEQs were calculated by setting all undetected and all EMPC-qualified results equal to zero. We observed that when EMPC values were retained, that 14% of the Site dioxin-TEQs from this area exceeded the LUT dioxin-TEQ of 0.912 mg/kg, whereas when zero was used for EMPC values, only 7% of the Site dioxin-TEQs exceeded the LUT dioxin-TEQ. Similar results were obtained when zero was used for all "undetected" results and when zero was used for all EMPC-results. The observed lower incidence of LUT exceedances when using zero for undetected results and EMPC values in the dioxin TEQ calculation suggests that this "zeroing" approach may aid in managing the uncertainty associated with false positives. Management of this uncertainty is particularly important when using the look up table process, which will involve many future single sample comparisons to the look up table value.

To manage the uncertainties associated with EMPC-qualified data, subsequent Site dioxin-TEQ calculations, and cleanup decisions using these results to discern exceedances near the LUT dioxin-TEQ, the DTSC-SSFL technical team agreed that zero should be used for EMPC-qualified data when calculating Site sample dioxin-TEQs. DTSC also believes that qualifying the EMPC values as non-detect is consistent with constraining the uncertainties associated with EMPC-qualified data. This conclusion is supported by the following observations:

(a) As established in the NFGs (see Section IX), the quality of EMPC data is suspect because it does not meet the range of ion mass to charge ratios required by Method 1613B (Section 10.2.2 in USEPA, 1994). This could result from the presence of an interference, or the presence of another compound. The NFGs recommend that the reviewer rely on professional judgment and organization policy to decide how to qualify EMPCs.

(b) Within the SA-5D study, in each case where the Site dioxin-TEQ exceeded the LUT dioxin-TEQ, more than 10% of each Site sample dioxin-TEQ was derived from J-flagged (estimated) values. Thus, exceedance of the soil screening value relies heavily on estimated data. The NFGs recommend that one consider the

impact of using estimated quantities in TEQ calculations. Sample-TEQs derived from any portion of "qualified (estimated) results" may also be listed as "qualified," and they cite an example of a J-qualified TEQ where 10% of the total TEQ is derived from J-qualified data (p 40 in USEPA, 2011). We sought to minimize reliance on estimated values for making cleanup decisions, particularly when cleaning up to method reporting limit levels, which have a reasonable degree of accuracy and precision (e.g., less uncertainty).

(c) From a health-protective standpoint, a LUT dioxin-TEQ of 1 pg/g soil represents a cancer risk of approximately 2E-7 based on comparison with the residential dioxin-TEQ Regional Screening Level of 4.9 pg/g (USEPA-Region IX, 2014). Thus, EMPC-qualified dioxin data that are, by their nature close to background, are of much less concern than are positively identified dioxin data at higher concentrations that coincide with significant cancer risks. So electing to set EMPC-qualified data equal to zero in sample dioxin-TEQ calculations is expected to have an insignificant impact on public health.

(2) **How are "non-detect" dioxin data to be evaluated in calculation of soil sample dioxin-TEQs?** In 2010, DTSC recommended to Boeing Co. that zero should be used for all Site-related "non-detect" dioxin results for purposes of calculating sample TEQs. The intent was to minimize false-positive results that would unnecessarily require soil cleanup. It is one of the goals of this memorandum to ensure that all Responsible Parties are being consistent in their calculation of Site sample dioxin-TEQs. Thus, the DTSC-SSFL technical team recommends that "zero" be used for all "non-detect" Site dioxin data for purposes of calculating the sample TEQ.

To ensure that dioxin results from the Chemical Soil Background Study (DTSC, 2012) were similarly treated, the DTSC-SSFL technical team examined how these background dioxin data were used to derive the LUT dioxin-TEQ. Comment #3 addresses these findings.

(3) **Confirmation of the LUT dioxin-TEQ of 0.912 pg/g:** In an April 2013 internal DTSC memo, HERO recommended that the LUT dioxin-TEQ be calculated on a "sample-basis." This means that dioxin-TEQs would be calculated for each of the 148 samples constituting the full Chemical Soil Background Study dioxin database, and that these results would be statistically evaluated to derive an upper threshold value on these data. Because the Administrative Orders on Consent (AOCs) for NASA and DOE require cleanup to background-based values, 95% Upper Simultaneous Limits (95% USLs) were chosen earlier to include all potential background data from the Background Study, excluding selected outliers. For 2,3,7,8-substituted CDD and CDF congeners, the 95% USL so calculated would thus represent the LUT dioxin-TEQ. For statistical evaluation, USEPA's ProUCL (v. 5.0) recommends that either detection limits (DLs) or reporting limits (RLs) be substituted for "non-detect" results, and that the "non-detect" observations be identified using "0" as an indicator variable to distinguish them from detected

observations, identified using a "1" indicator variable (Section 1.14.1, USEPA, September 2014).

The DTSC-SSFL technical team confirmed that the LUT dioxin-TEQ was calculated using the congener method, rather than on a sample basis. That is, data for each set of 17 2,3,7,8-substituted CDDs and CDFs presented in the Chemical Soil Background Study dataset were statistically evaluated to derive 95% USLs for each congener. As discussed in Section 5.2.2 (Non-Detects, "U"-Flagged Data, and "J"-Flagged Data) and listed in Table 5 of the Chemical Soil Background Study Report, Method Detection Limits (MDLs) were substituted for non-detects (NDs) prior to statistical evaluation (DTSC, 2012). Each 95% USL BTV was then compared with the Minimum Reporting Limit (RL_{min}) for each congener, as specified in Table 4 of Appendix B (Quality Assurance Project Plan (QAPP)) to DTSC's Chemical Soil Background Study: Sampling and Analysis Plan, and the greater value between the two was selected (DTSC, May 2011). Each of twelve congener-specific 95% USL BTVs and five RL_{min}'s was multiplied by its respective TEF to yield a congener-specific Toxicity Equivalent Concentration (TEC), then all TECs were summed to yield the overall LUT dioxin-TEQ.

To confirm the LUT dioxin-TEQ using the congener approach, HERO reconstructed dioxin congener TECs by multiplying each congener-specific TEF by the above selected 95% USLs or RL_{min}'s. The sum of these congener-specific TECs yielded a congener-based dioxin-TEQ of 0.924 pg/g, which is close to the LUT dioxin-TEQ of 0.912 pg/g. The difference between these two values may have been attributable to rounding errors used in this recalculation.

For comparison purposes, HERO then calculated a sample-based dioxin-TEQ using the Chemical Soil Background Study dioxin database. To be consistent with the congener-based dioxin-TEQ determination, estimated detection limits were substituted for non-detected congener results. Sample-specific TEQs were derived for each of 148 background soil samples by multiplying dioxin congener concentrations by their respective TEFs, then summing the resulting TECs to yield each sample TEQ. Using Pro-UCL (v. 5.0) software, the background sample TEQs were statistically evaluated to derive a 95% USL. As summarized on Table 1 below, ProUCL identified these data as being consistent with a gamma distribution, and two 95% USLs were recommended, a Wilson-Hilferty (WH) 95% USL of 0.963 pg/g, and a Hawkins-Wixley (HW) 95% USL of 1.03 pg/g. The WH and HW 95% USL values were derived by first transforming the Chemical Soil Background Study dioxin dataset from a gamma distribution to a dataset that was consistent with a normal distribution (USEPA, 2014). Both HW and WH methods utilize similar but slightly different transformation functions that yield comparable upper threshold limits for mild to moderately skewed gamma distributions.

Table 1. Summary of LUT Dioxin-TEQ Calculations and Conditions Used

Wilson-Hilferty (WH) 95%USL	Hawkins-Wixley (HW) 95%USL	Other 95%USL	ProUCL Statistical Distribution Used	Outlier(s) Sequestered	Number of Sample Data Used for TEQ	Substitution for "NDs"	Substitution for J-Flagged Data
0.963	1.03	--	Gamma	none	148	EDLs	none
0.908	0.973	--	Gamma	1	147	EDLs	none
1.022	1.127	--	Gamma	none	148	0	none
0.967	1.069	--	Gamma	1	147	0	none
--	--	1.085	Non-parametric*	none	148	0	MRL
--	--	0.686	Non-parametric*	1	147	0	MRL

Abbreviations: EDLs = estimated detection limits; MRL = method reporting limits; NDs = non-detects.
All duplicates averaged.
* Per ProUCL, no discernable distribution.
Important Consideration: Approx. 90% of individual background sample TEQ values were calculated using ≥ 10% J-flagged congener data.

Based on ProUCL graphical results and use of the Rossner test for outliers, one background sample TEQ (TEQ=1.085 pg/g) was identified as an outlier. When this outlier was removed and the remaining 147 background sample TEQs statistically analyzed, ProUCL again concluded that the data were consistent with a gamma distribution, and it recommended a WH 95% USL of 0.908 pg/g and an HW 95% USL of 0.973 pg/g (Table 1). Thus, there was only a minimal difference between the WH 95% USLs and the HW 95% USLs that were recommended by ProUCL, whether or not the single outlier was sequestered prior to the USL determination. And, the WH 95% USL of 0.908 pg/g essentially confirmed the congener-based LUT dioxin-TEQ of 0.912 pg/g, where the single outlier had been sequestered and detection limits were substituted for non-detects for both analyses. Cumulatively these USL results, which all fall into a relatively narrow range regardless of which transformation was used and whether or not outliers were included, demonstrate the robustness of the dioxin/furan background dataset.

To be consistent with HERO's recommendation in comment #2, the 95% USL dioxin-TEQ was also calculated for the Chemical Soil Background Study dataset with zero substituted for non-detects, and with and without sequestration of the single outlier value. ProUCL again concluded that these background dioxin-TEQ datasets were consistent with gamma distributions, and it recommended WH 95% USLs of 1.022 pg/g (n=148; outlier included in data evaluation) and 0.967 pg/g (n=147; outlier sequestered from dataset), and HW 95% USLs of 1.127 pg/g (n=148; outlier included in data evaluation) and 1.069 pg/g (n=147 pg/g; outlier sequestered

from dataset; Table 1). Because DTSC went to significant efforts to ensure that the Chemical Soil Background Study was completed in areas considered unimpacted by anthropogenic sources, the DTSC-SSFL technical team found no justifiable reason to exclude the background TEQ identified as a statistical outlier. Therefore, we recommend use of either the WH 95% USL of 1.022 pg/g or the HW 95% USL of 1.127 pg/g as an appropriate background dioxin-TEQ. To resolve which of these two dioxin-TEQs should be chosen, the DTSC-SSFL technical team contacted a leading statistician who contracts with the USEPA. She stated that there are currently no criteria for choosing the WH 95% USL over the HW 95% USL, or vice-versa. In the interest of minimizing false positives, and recognizing that a LUT dioxin-TEQ close to 1 pg/g is still health-protective, and that each of the WH and HW 95% USLs listed in Table 1 rely on estimated analytical results, the DTSC-SSFL technical team recommends the dioxin-TEQ of 1.127 pg/g be used as an updated estimate that better represents the background dioxin TEQ population.

Finally, consistent with NFG guidance (see p 3, item (b)) we sought a method to reduce the uncertainty involved in using more than 10% J-flagged congener data to calculate the background dioxin-TEQ. Although no clear choice appeared better than using the laboratory derived J-flagged estimated congener concentrations, we chose to assign an upper-limit to the J-flagged data to determine how the 95% USL would be affected. J-flagged data are defined as positive identifications of the analyte where the concentration is approximated because either certain QC criteria are not met, or the analyte concentration is below the adjusted Contract Required Quantitation Limit (CRQL; NFG, 2011). All J-flagged dioxin congener data in the Soil Chemical Background dataset were replaced with Method Reporting Limit (MRLs) for respective dioxin/furan-congeners. A value of zero was substituted for non-detected results. The MRL-substituted dioxin background dataset was then evaluated using ProUCL. ProUCL concluded that the MRL-substituted dataset was not consistent with either a normal, lognormal or gamma-distribution. Therefore, ProUCL selected the highest background sample dioxin-TEQ as the 95% USL, ie, 1.085 pg/g using the complete dataset (n=148) and 0.686 pg/g where the single statistical outlier of 1.085 pg/g was sequestered (n=147; Table 1). Because this approach selects only the maximum value in a dataset, it is less preferred than a 95% USL derived using a defined distribution, such as gamma distribution, which uses the entire dataset. Therefore, the DTSC team concluded that substitution of MRLs for J-flagged data was a highly conservative assumption, and thus not recommended. Our recommendation for a background dioxin-TEQ of 1.127 pg/g was retained.

(4) **Summary:** Based on the above outcomes, the DTSC-SSFL technical team makes the following recommendations:

(a) EMPC-qualified and Non-detect Data: For the purpose of calculating a sample dioxin-TEQ, both EMPC and other non-detect data should be substituted with the value of zero. The actual data remain within the laboratory data report

regardless of the TEQ calculation requiring a zeroing effort. This applies to all sample dioxin-TEQ calculations, whether for background or site-related data.

(b) **Current LUT Dioxin-TEQ:** The DTSC SSFL technical team confirmed that the current LUT dioxin-TEQ of 0.912 pg/g was derived using a congener-based approach. Using comparable assumptions (ie, substitution of Estimated Detection Limits for non-detects and sequestration of the single sample dioxin-TEQ statistical outlier [ie, 1.085 pg/g] from the background dataset), HERO calculated a sample-based dioxin-TEQ of 0.908 pg/g (ie, Wilson-Hilferty 95% USL in Table 1). These values are essentially identical.

(c) **Alternative LUT Dioxin-TEQ:** To be consistent with calculation of sample dioxin-TEQs determined from Site data, the DTSC-SSFL technical team recommends that the LUT background sample-based dioxin-TEQ be calculated similarly. That is, non-detects should be set to zero. Because sequestration of the single statistical outlier from the background sample-based dioxin-TEQ dataset could not be adequately justified, the DTSC-SSFL technical team recommends that all 148 sample TEQs be used in the derivation of the background LUT dioxin-TEQ. As shown in Table 1, this results in a Wilson-Hilferty (WH) 95% USL of 1.022 pg/g or a Hawkins-Wixley (HW) 95% USL of 1.127 pg/g. Although criteria do not exist for choosing either the WH 95% USL over the HW 95% USL, or vice-versa, the DTSC-SSFL technical team recommends that the HW 95% USL of 1.127 pg/g be selected as the background dioxin-TEQ to help minimize potential impact of false positives and to minimize reliance on J-flagged (estimated) dioxin-congener results for calculation of background sample TEQs, and to make use of all background dioxin-TEQ data.

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